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/THE FUNCTIONALITY OF A CHLORINATED SOFT WHEAT  
FLOUR IN A COOKIE SYSTEM/

by

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Dedicated with  
love to  
Garry Banning

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## INTRODUCTION

History shows that as early as 1914 (Utt, 1914) chlorine-treated flours were used in bakery products. Initial use of chlorine in flour milling was to bleach and mature bread flours (Monzheimer, 1931). Bread flour is no longer treated with chlorine due to the advent of new and improved bleaching and maturing agents, e.g., benzoylperoxide and azodicarbamide (ADA), respectively.

Chlorinated flour has been used in the production of cakes for a long time. The chlorinated flour serves several purposes in cakes. The chlorine treatment of flour allows high levels of sugar and shortening in proportion to flour. For many U.S. consumers, the richer the cake the better it tastes. Chlorinated flour prevents collapse of richer-type cake structures during baking and subsequent cooling. Cakes prepared with treated flour have higher volume, improved eating quality and finer crumb grain. (Johnson et al, 1979).

Although Harrel (1952) noted that chlorination of flour reduces cookie diameter, recently chlorine-treated flour has been used in the cookie industry. The treatment of flour with chlorine controls the cookie diameter to better meet packaging specifications.

Chlorine treatment of flour then, has a number of different baking applications that may either improve or control certain characteristics desirable in flour-based bakery products. The improving effect of chlorine-treated flour on bread, cakes, and to certain degree on cookies illustrates the multiple potential of chlorine as a diverse modifier of flour functionality. Recently, interest has centered on the mechanism of the improving action of chlorine and the nature of the underlying



chemical changes.

The objective of this study was to define the functionality of chlorinated flour in a sugar snap cookie formulation and more specifically to determine how the use of chlorine-treated flour influences cookie dough rheology, baking performance, and cookie quality characteristics.

## LITERATURE REVIEW

Previous studies with chlorinated flour were primarily limited to its application, and elucidation of its improvement, in cake systems. There is little information concerning the mechanism of functionality of chlorinated flour in cookies. Chlorine-treated flour is, in general, used in the cookie industry to control cookie spread. The flour used by cookie manufacturers is treated with higher chlorine levels than those flours produced for cake production. Most cake flours are treated to a pH between 4.6 and 4.8, whereas, cookie flours are treated with chlorine to a pH of 4 or less and then blended with other streams of cookie flour to give a pH of 4.5.

Although cookies were the subject of several recent theses (Curley, 1984; Abboud, 1984; Doescher, 1985), no attention was given to the use of chlorine-treated flours. In cakes the action of chlorine is thought to affect the starch component by oxidation and depolymerization (Urchino et al, 1962; Whistler et al, 1966). These changes result in strengthening of the cake structure during baking. However, since starch does not undergo gelatinization in cookies, a different improving mechanism may be operative in formation of cookie structure. Consequently, the mechanism suggested for cakes may not be applicable to cookies. In elucidation of the action of chlorine, one has to remember that chlorine acts on many components of flour, e.g., starch, protein, lipids, and pentosans.

One of the first to report a deleterious effect of chlorinated flour in cookies was Alexander (1939). He observed that cookies made with chlorine-treated flour lacked spread, top grain, and crispness.

Flours treated with chlorine were observed to give somewhat sticky doughs, which are not easy to handle and mold (Alexander, 1939). He also attributed this sticky dough to the gluten being in a "colloidal" state preventing dough formation. Other workers in this field (Harrel, 1952; Sollars, 1958) also reported deleterious effects of chlorine-treated flour on cookie diameter and top grain quality. The cookie baking quality of flour is measured directly by cookie diameter, so chlorine does not improve cookie flours but is useful in controlling cookie size to meet packaging specifications (Harrel, 1952). Sollars (1958) reported on effects of fractions derived from chlorine-treated cookie flour on cookie spread. He separated three flours, both bleached and unbleached, into water solubles, gluten, tailings, and prime starch fractions by a modified acetic acid fractionation procedure. For chlorine bleached cookie flours, major responses in cookie diameter were consistently attributed to chlorine-treated gluten and prime starch fractions, other fractions were found to give only occasional, small responses (Sollars, 1958).

#### Actions of Chlorine on Starch

Starch constitutes the major fraction of flour by weight. The action of chlorine upon starch may be considered as two separate, but not necessarily unrelated, events. In a critical review of the functionality of chlorine in high ratio cake flour, Gough et al (1978) stated that reactions may occur with the individual amylose and amylopectin molecules, or the granule, as a structural unit. Experimental evidence for chemical attack on starch at relatively low chlorine concentrations (i.e. those used in the chlorination of cake flour) is limited (Johnson et al, 1979). Most studies are concerned

with those changes occurring at high concentrations (greater than 1% chlorine based on starch), in excess water, and at low pH.

Most notable of the investigations on the interaction between starch and chlorine has been that of Urchino et al (1962) and Whistler et al (1966). Their studies led to the proposal of a mechanism for the breakdown of starch molecules through oxidation and depolymerization. Reactions were conducted both in an aqueous chlorine-starch slurry and in the presence of a limited amount of water. The former reaction (chlorine-starch slurry) showed that extensive depolymerization occurred, along with extensive oxidation of the D-glucosidic carbons C2 and C3, inducing ring opening and transformation of carbons C2 and C3. An extensive depolymerization ensued because of the cleavage of glycosidic bonds, which also led to the formation of large amounts of D-glucose and D-gluconic acid, as chain end units and free molecules. In limited water, this reaction was greatly diminished. This study was conducted at much higher levels of chlorination than normally used in flour.

#### Action of Chlorine on Protein

Only limited chemical evidence exists on the nature of the chlorine-protein reactions occurring in flour, but the fact that some change does take place is demonstrated by the unsuitability of chlorinated cake flour for bread making purposes. A detailed analysis by Ewart (1968) of flour treated with chlorine at a level of 50 oz./sack (11,000 ppm) showed measurable changes in the amino acids of the gluten. In addition, 20% of the amide groups were hydrolyzed, and some disulfide and peptide bond cleavage occurred. Tsen et al (1971) also found evidence of chlorine reactions with tyrosine and sulfhydryl groups.

### Action of Chlorine on Lipids

Flour lipids can undergo two types of reactions with chlorine: oxidation and chlorine addition. Oxidation will disrupt the fatty acids at double bonds to form fragments containing carbonyl groups. Chlorine combines with unsaturated fatty acids at the double bond. Both reactions will reduce the level of unsaturated fatty acids. It has been observed that, at pH values above 4.0, oxidation predominates by Kulp and Ke, (1981). They also postulated that the intermediates of lipid oxidation (peroxides) indirectly oxidize flour starch.

### Action of Chlorine on Other Flour Components

Many past studies on the chlorine bleaching of wheat flours have been concerned with the effect of chlorine on the starch fraction with fewer studies concentrating on the hemicelluloses. Even though one flour component may react with only a small proportion of the chlorine, the contribution of the altered component to flour characteristics may be significant.

Polysaccharides strongly influence the rheology of flour doughs (Cole, 1968). The results of Cole (1968) show that wheat-flour hemicelluloses, mainly xylan with arabinose side chains, are affected by chlorine bleaching. The arabinose side chains are split off in the early stage of this reaction, leaving a stable insoluble xylan. As a result of this reaction, the rheological and water absorbing capacity of a wheat flour is altered (Cole, 1968).

### Cookie Bake Test

Finney et al (1950) developed a micro cookie baking test that produced 2 cookies using only 40 g. of flour instead of the 225 g previously required. That test has been used for quality evaluation of

flours because it is: simple, easy to perform with sufficient accuracy, reproducible, and because it accurately reflects variations in flour characteristics (Yamazaki, 1954). This cookie bake test is probably the best single means available for evaluating the suitability of soft wheat for cookie production. Quality in this test is synonymous with large cookies with open and well-developed cracks.

#### Analytical Methods

Much of the work on cookie flour quality has been concerned with analytical values. Flours were analyzed for moisture, ash, and protein. Good cookie flours are usually, but not always, low in protein, ranging from about 7 to 8% protein (Yamazaki, 1959). The amount of chlorine required to reach a desired pH level varies with the ash, moisture, and protein values (Kulp et al, 1985). Sollars (1958) found that changes in chlorine requirements to reach a certain pH must be almost entirely due to changes in the protein of the bleached flour.

#### Physicochemical Studies

Physicochemical tests include such tests as the farinograph, alveograph, viscograph, falling number, differential scanning calorimeter, etc. The farinograph measures rheological properties of dough during mixing. The alveograph measures rheological properties of precut and rested dough pieces. The farinograph is the most universally used physical dough testing instrument to measure plasticity and mobility of dough. The farinograph has been used extensively for evaluating flours in the past. Two important physical dough properties that can be seen with the farinograph are: 1. The absorption or amount of water required for a dough to have a definite consistency. 2. A general profile of the mixing behavior of the dough. The alveograph reveals

information about the dough handling property and dough extensibility.

Measurements of viscosity by the amylograph can provide a useful indication of pasting properties in more concentrated starch-water systems. Amylograms of treated flour revealed that chlorination slightly accelerated the rise in viscosity between 50 and 75°C, but did not affect the final peak viscosity unless very high doses were used (Kulp et al, 1972). Miller et al (1973) found that chlorination suppressed granule folding, and inhibited the release of an exudate (presumably amylose) and, therefore, viscosity development.

The gelatinization temperature microscopically measured as loss of birefringence in 50% of the granules on a Kofler hot stage was not affected by chlorine treatment of flour (Kulp et al, 1972; Cauvain et al, 1975). This observation appears to be supported by most workers in this field. When Miller et al (1973) heated appropriately dilute starch slurries in the amylograph and periodically examined the starch microscopically, they found there was no apparent difference between the granules of the treated and control samples during the initial phase of gelatinization. Once above 70°C, the swollen control granules "folded" but, this phenomenon was apparently suppressed by chlorination (the starch was bleached to pH 2.5 to 2.9). This brief review of literature indicates necessity for investigation for the mechanism of chlorine-treated flour in cookie systems.

## MATERIALS AND METHODS

### Materials

Flour. A commercially milled soft wheat cookie flour was bleached with 1 to 16 oz/cwt [0.0626 to 1.00 g of chlorine per 100 g of flour] by the Pennwalt Corp. Flour Service, Buffalo, NY. Flour protein (N x 5.7) and ash contents were 8.3% and 0.39% respectively, (14% m.b.).

### Methods

Chlorination Treatment. Flour was chlorinated by Pennwalt Corporation as noted above in a Wallace and Tiernan laboratory bleacher using liquid displacement of chlorine gas to control the treatment level.

Analytical Tests. Moisture, pH, protein, and ash were determined according to AACC procedures (1976) methods 44-15A, 02-52, 46-12, and 08-01 respectively.

Isolation of Starch. Starch was isolated from untreated and treated flour. One part flour to one part water by weight was mixed to produce a dough, in a Hobart (Model A-120) mixer. The starch was then washed from the dough by stirring in three batches of excess water for 10 minutes each. The starch suspension was centrifuged at  $3000 \times g$  for 15 min using a IEC EXD centrifuge. The sediment contained two layers. The bottom one was prime starch and the top layer was tailings containing small starch granules, protein, pentosans, and endosperm cell wall material. Tailings were scraped off, combined, resuspended and recentrifuged to improve the starch recovery. Prime starch was exhaustively washed with distilled water, then air dried in a continuous flow of room temperature air.



Farinograph. Farinograms were prepared using untreated and flour treated with various levels of chlorine according to AACC procedure number 54-28A (50 g bowl), (1976).

Alveograph. The alveograph method of Chopin, (1960) was employed. Measurements were made from the mean of the alveograph curves made with the MA 82 alveograph.

Cookie Dough Consistency. The method of Olewnik and Kulp (1984) was used to test dough consistency. All doughs were prepared in a National mixer using Finney's Micro Method III procedure and formula (see Cookie Baking) with untreated and flours treated with various chlorine levels.

Dough consistency (stiffness) and band width (cohesion) were recorded with a Brabender farinograph equipped with a 50 g bowl. Tests were run for 15 min. The horizontal position of the band on the chart was considered a measure of consistency (resistance to movement). A larger BU value indicates a stiffer dough. The band width was considered a measure of degree of tenacity or cohesive properties of doughs.

Cookie Dough Stickiness. The method used to test dough stickiness followed a procedure by Curley and Hosenev (1984) with some modifications. Dough stickiness was measured on the Instron Universal Testing Machine (Table Model TM) in the tension mode. The Instron was set to give a full scale force of 2 kg. The head speed was set at 12 mm/min and the chart speed set at 500 mm/min. Dough samples were compressed by a constant force of 1 kg with a brass plunger of 21.5 mm diameter. The area under the tension curve was measured with a planimeter and reported as dough stickiness in  $\text{cm}^2$ .

Cookie dough was prepared with 5 different levels of chlorinated flour according to Finney's Micro Method III procedure. After mixing, the dough was completely covered to prevent surface drying and left to equilibrate for approximately 10 min. Dough was sheeted and cut with cookie cutter (60 mm i.d.). The cookie cutter was left in place to prevent spreading of dough during compression. This procedure was found to be reproducible and stickiness was reported as an average of three measurements.

Differential Scanning Calorimetry (DSC). A Perkin-Elmer DSC-2 (Perkin-Elmer Corporation, Norwalk, CT) with an Intra Cooler II was used to measure starch phase transitions in simple systems (starch and water). The DSC was calibrated with distilled water and indium.

Starch isolated from untreated and varied levels of chlorine treated flour was weighed (approximately 3 mg), transferred to preweighed aluminum DSC pans, and excess distilled water was added to allow for gelatinization. Pans were sealed, reweighed and allowed to equilibrate for 30 min at room temperature. The sample was then placed in the DSC sampling block. An empty pan was used as a reference.

The samples were cooled to 7°C and then heated to 127°C at a rate of 10°C/min; a sensitivity of 0.5 mcal/sec and a chart speed of 10 mm/min were used.

The thermograms obtained were used to determine the transition temperature and the enthalpy of transition. The area under the curve was integrated by means of a planimeter. Indium was used as a standard for enthalpy calculations.

Heat of transition  $H$ , was calculated according to the formula.

$$H \text{ sample} = 6.8 \times \frac{\text{wt indium}}{\text{wt sample}} \times \frac{A \text{ sample}}{A \text{ indium}} \times \frac{R \text{ sample}}{R \text{ indium}} \times \frac{S \text{ indium}}{S \text{ sample}};$$

where H = heat of transition (cal/g); wt = weight (mg); A = area under curve; R = range sensitivity (mcal/sec); and S = recorder chart speed mm/min.

#### Sample Preparations for Scanning Electron Microscope (SEM).

Cookie Crumbs. Cookies were ground in a Quaker City Mill Model 4-E Philadelphia, PA and defatted with petroleum ether in a Soxhlet extractor for 9 hr.

Cookie Dough. Samples of cookie dough were rapidly frozen by immersion into methyl butane cooled in liquid nitrogen and freeze dried at  $-60^{\circ}\text{C}$  for 48 hr in an Edwards ETD1 freeze dryer.

Scanning Electron Microscopy of Cookie Samples. The prepared cookie samples were sprinkled onto double-sided adhesive tape attached to specimen stubs; they were coated with gold-palladium (60-40) by high vacuum-evaporation. Samples were viewed with a Perkin Elmer ETEC U-1 Autoscan scanning electron microscope. Images were photographed on Polaroid film type 55 PN at magnifications of 500 and 1,000x.

Determination of Starch Gelatinization Temperature Ranges. Loss of birefringence, swelling power, and gelatinization temperature ranges were determined for starch isolated from bleached and unbleached cookie flours. A Kofler hot stage in conjunction with a microscope was used to aid in these determinations. The recorded temperatures corresponded to loss of birefringence by 5, 50 and 95% of the granules (MacMasters, 1964).

Amylograms. Pasting characteristics of cookie crumbs baked with untreated and various levels of chlorine-treated flour were prepared on

a Brabender Amylograph model VA-VE (C.W. Brabender Inc., South Hackensack, NJ) using the rapid amylograph method with the following modifications.

The amylograph was calibrated against a standard starch curve supplied by Brabender Corporation. Cookies previously made with untreated and various levels of treated flour were crumbled and 32 g (14% m.b.) were placed in a 250 ml Erlenmeyer flask. Added to the flask was 70 ml distilled water of the premeasured 90 ml. The slurry was shaken 50 times in 30 seconds. The cookie slurry was poured into the Amylograph sample bowl. The flask was rinsed with the remaining 20 ml of distilled water and added to the cookie slurry in the bowl. The minimum height in BU peak was recorded as maximum consistency.

Falling Number Determinations. Falling number was determined on the control and chlorine-treated flours according to AACC procedure number 56-81B. (A falling number AB Norlandsgatan 16, Stockholm, Sweden was used for determination.) Samples were run in duplicate with averages reported in seconds (sec).

Cookie Baking. Cookies were baked (formula in Table 1) from untreated and treated flour (0-16 oz chlorine per cwt of flour) using the Micro Method III procedure of Finney et al (1950). Two cookies were cut from each dough using a cookie cutter (60 mm i.d.) then baked in a reel oven for 10 min at 204°C. Duplicate samples were run with each level of chlorine treatment. Mean cookie diameter and thickness were measured for each sample from the untreated and each level of chlorine-treated flour.

Table 1. Cookie Formula

Ingredient	Bakers %
Flour	100
Sugar	60.0
Shortening	30.0
Nonfat Dry Milk Solids	3.0
Sodium Bicarbonate	1.80
Ammonium Chloride	0.55
Salt	0.45
Water	16.8

## RESULTS AND DISCUSSION

It was the objective of this study to elucidate the mechanism by which chlorinated flour affects the spread of cookies and the rheological properties of the dough. A control flour and flour treated with various levels of chlorine were studied by rheological methods. Physicochemical methods and SEMs were used to study the starch fraction of treated flours. Cookies were baked to demonstrate the effect of chlorinated flours on the cookie spread factor.

### Analytical Tests

Protein and ash of the first batch of flour received was 8.3%, and 0.39%, respectively, (14% m.b). Protein and ash of the second batch was 8.1%, and 0.40% respectively, (14% m.b.). The pH value of all samples are listed in Table 2.

Normally, flour has a moisture content of 13.0 to 15.5% (Kent-Jones and Amos, 1967). Therefore, chlorine may readily dissolve in this flour-water system giving:



The rapid drop in pH observed as the level of chlorination increased is due to the formation of hydrochloric acid as observed by Ferrari and Bailey (1929) and Hanson (1932). The HOCl is a powerful oxidant, which reacts further with flour components.

### Effect of Chlorine on the Rheological Properties of Flour.

#### Farinograms

The farinogram curves (Fig. 1) demonstrate increases in dough stability with chlorine treatment levels up to pH 3.9, followed by a rapid weakening of the doughs at higher chlorine levels. This same

Table 2. pH of Water Suspension of Flour  
Treated With Chlorine

Chlorine Treatment Level oz/cwt Flour	pH of Suspension
0	5.8
2	4.7
4	3.9
8	2.3
16	1.4

Figure 1. Effect of degree of chlorination on farinograms.



CONSISTENCY (BU)

pH FLOUR = 5.8  
ABS. = 48.5

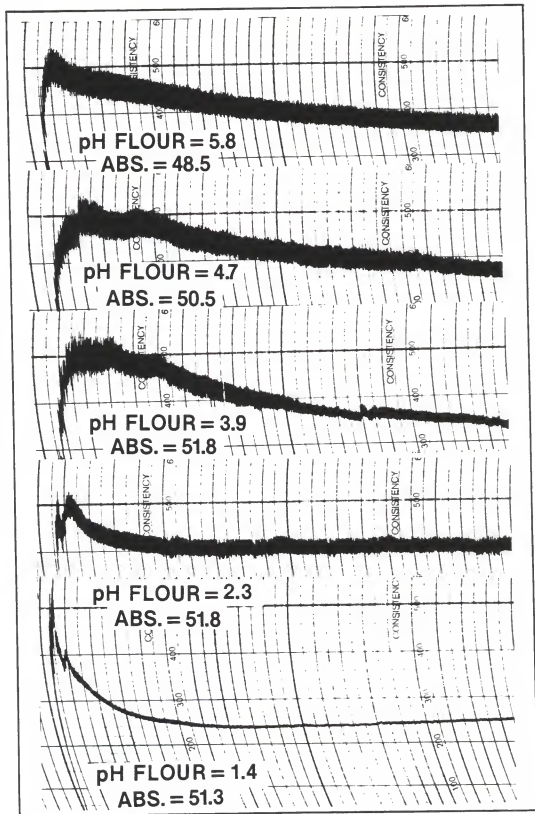
pH FLOUR = 4.7  
ABS. = 50.5

pH FLOUR = 3.9  
ABS. = 51.8

pH FLOUR = 2.3  
ABS. = 51.8

pH FLOUR = 1.4  
ABS. = 51.3

TIME (MIN)



trend is also evident from the mixing tolerance of the doughs. Departure time from the 500 BU line is longer for the 2 and 4 oz chlorine per cwt treated flour but very little time is needed for the 8 and 16 oz chlorine per cwt flour to depart from the 500 BU line.

The strengthening of the doughs with up to 2 oz. chlorine per cwt of flour is attributable to the oxidation of the sulfhydryl to disulfide groups of the flour proteins. The further weakening of flour proteins at higher chlorine treatments (4-16 oz chlorine per cwt of flour) is due to cleavage of peptide bonds in high molecular weight proteins, leading to smaller fragments. Reactions of the cleavage type are consistent with increases in protein solubility observed with chlorination (Tsen, 1971).

With each increment of chlorine treatment to pH 3.9, an increase in water absorption of the flour was observed. Chlorination of flour produces cleavage of secondary bonds producing conformational changes in the gluten resulting in a greater capacity for taking up water. The hydration capacity of the starch also increases (Alexander, 1939). Other factors affecting absorption of chlorinated flours are cleavage in starch granules at high levels of chlorine treatment (Kulp et al, 1972) and degradation of pentosans (Cole, 1968).

#### Alveograms

The alveograms (Fig. 2) reveal information about the gluten strength and the state of oxidation of the untreated and chlorine-treated flour. Measurements taken from the curves (Table 3) show the height (H), the water absorbing capacity of the flour (P), length (L), and the mechanical work (W) necessary to blow the bubble. The height of the curve is a good indicator of how strong or weak the dough has

Figure 2. Effect of degree of chlorination on alveograms.

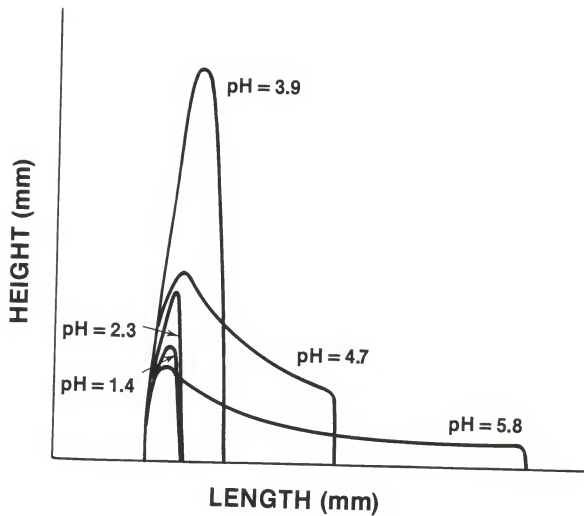


Table 3: Alveogram Indices

pH Flour	Length (mm)	Height (mm)	P (mm)	W ( $10^{-4}\text{J}$ )
5.8	135	31	35	123
4.7	60	63	69	185
3.9	27	133	146	328
2.3	11	57	62	132
1.4	10	40	44	109

become (Khattak et al, 1974) or to what extent oxidation and protein cleavage has proceeded. As the level of chlorination increased so did the resistance of the dough to extensibility as shown by alveograph measurements up to pH 3.9.

At the two highest levels of chlorination pH 2.3 and 1.4, the dough rapidly weakened, became sticky and was difficult to extract from the machine which was attributed to cleavage of peptide bonds in the gluten proteins.

The extensibility of the dough (L) showed the control flour (pH 5.9) had the greatest resistance to extensibility. With each increment of chlorine treatment, the dough lost extensibility. This loss in extensibility correlated well with extensigrams of flour of similar pH (Kulp et al, 1985).

The water absorbing capacity of flour (P) was in good agreement with the farinograms. Water absorption increased to pH 3.9 and decreased at a higher level of pH (2.3 and 1.4).

The work (W)  $\times 10^{-4}$  J which is necessary to rupture the bubble, increased to pH 3.9. As flour chlorination treatment increased to the highest level, or flour pH 1.4, the dough lost all cohesive properties as indicated by the very small amount of work required to rupture the bubble. This was conducted without pH adjustment of flour.

#### Cookie Dough Consistency

Optimum cookie dough consistency from flour to flour should vary within a narrow range. A starting guide for the amount of water, relative to soft wheat flour protein values needed for optimum dough consistency, is given in a table of the Micro Method III (Finney, 1950). According to this estimate, an additional 0.8 ml water (over the water

provided from liquid ingredients and flour moisture) is necessary to produce a dough with optimum consistency for a flour of 8.3% protein.

The change in dough consistency attributable to chlorination was demonstrated by a modified farinograph procedure (Olewnik and Kulp, 1984). Appropriate amounts of cookie dough from flours of varied chlorination were prepared according to Finney's Micro Method III (1950) and measured for variation in consistency by recording the resistance of the blades to the developed dough.

These farinograms are shown in Fig 3. Initial dough consistency for all flours was similar but there was an appreciable effect on the mixing stability of the dough. The consistency of the cookie dough made with flour (pH 5.8) had the greatest stability. With each increment of chlorination the cookie dough consistency decreased. This was done without pH adjustment of flour.

Initial dough consistency was similar when water was decreased from 0.8 to 0.4 ml, but there was an appreciable effect on mixing stability. The decrease in water level produced doughs with lower cohesiveness but similar stability as those with lower absorption water.

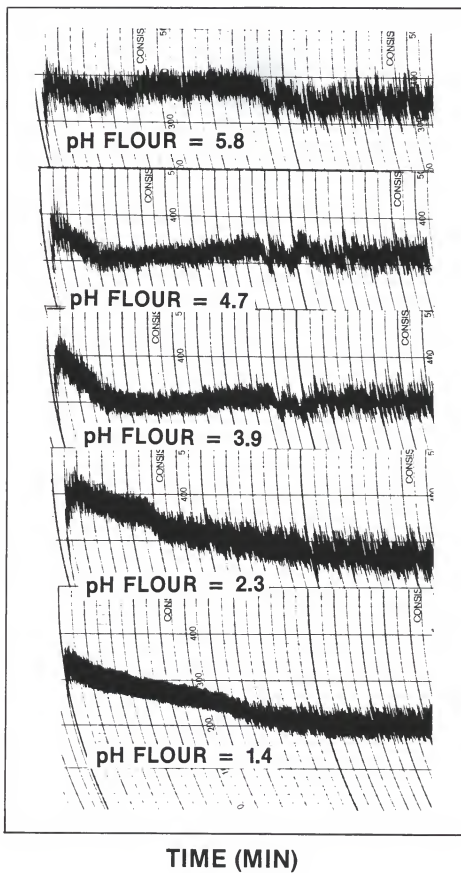
#### Cookie Dough Stickiness

As consistency was observed to decrease, the stickiness of the cookie became stickier. Stickiness of the dough was subjectively evaluated by observing the adhesion to the rolling pin of the dough made from each level of chlorine-treated flour. Excessive dough stickiness was detected in doughs from flours treated with 8 and 16 oz chlorine per cwt of flour. Flours from the lower level of chlorination (0, 2, and 4 oz chlorine per cwt of flour) did not produce doughs with near the stickiness seen in the highest chlorine-treated flour.

Figure 3. Effect of degree of chlorination on cookie dough consistency.



CONSISTENCY (BU)



The two curves shown in Fig. 4 represent doughs made with 0 oz chlorine per cwt of flour (dotted line). The cookie dough made from untreated flour (0 oz chlorine per cwt of flour) was firm and manageable and during its measurement on the Instron the plunger made a quick and clean release from the dough. The 16 oz chlorine per cwt of flour (solid line) was sticky and during its measurement on the Instron, the plunger released slowly and carried some dough with it. With each increment of chlorination the area under the tension curve increased. As reported by Curley and Hoseney (1984) adhesive forces between dough and plunger are greater than cohesive forces within the dough.

Cookie doughs containing increasing increments of chlorinated flour from 0 to 16 oz chlorine per cwt of flour showed a concurrent increase in dough stickiness with each increase in flour chlorination (Fig. 5). The increased stickiness of doughs made from flour treated with chlorine was a soft wheat testing problem encountered by Alexander (1939). He found that the chlorination of cookie flours reduced the plasticity of dough making it difficult to handle.

#### Polarized Microscopy

Starch samples from the untreated and chlorine-treated flour were wetted and viewed under the microscope to observe the external microscopic form, birefringence, and were then heated to determine gelatinization temperatures. In the starch samples viewed (isolated from 0-16 oz chlorine per cwt of flour) all exhibited identical external microscopic form and characteristic polarization crosses. The gelatinization temperature ranges are shown in Table 4. The temperature of gelatinization increased at higher levels of chlorination (above 4.0 oz per cwt). This observation is analogous to Kulp et al (1972). The change

Figure 4. Instron tension curves for dough stickiness.

Dotted line shows 0 oz chlorine per cwt of flour.

Solid line shows 16 oz chlorine per cwt of flour.

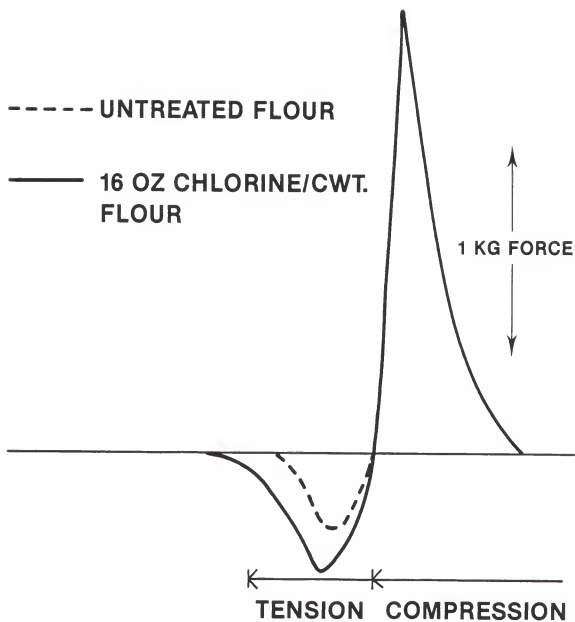
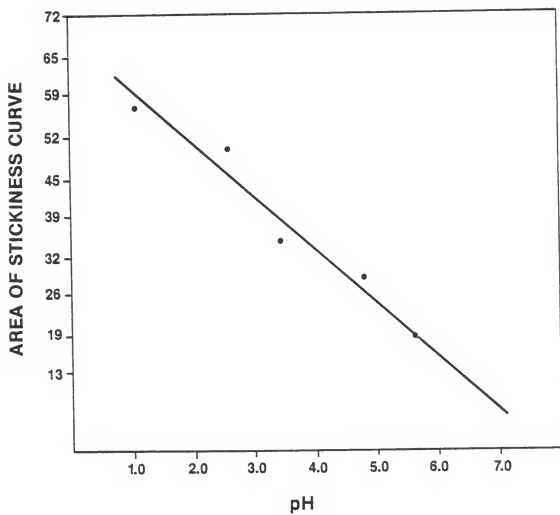


Figure 5. Relationship between dough stickiness as level of chlorine treated flour increased.  $r = ^{-}0.97$ .



in gelatinization temperature at high acidities (below pH 3.9) are attributed to cleavages in the crystalline order of the granules. This is supported by further experimental evidence (DSC, viscograph) given in the following discussion.

In these tested samples what does seem important is the rate and degree of granule swelling after gelatinization. There was a minimum number of imperfect starch granules (1:200) in both samples isolated from low to moderately chlorine-treated flour and those from untreated samples. Only the starch from highly treated flour showed a different behavior during gelatinization and swelling. Gelatinization temperature range of that sample was about 4° higher than that of the control and lower chlorine-treated samples. In the microscopic specimen of this starch from flour pH 1.4, more eroded starch granules were seen. However, even granules which showed erosion were birefringent and gelatinized normally. After gelatinization, the starch granules from the highly treated flour did not show a normal swelling pattern as observed in the other samples, but started to disintegrate without prior swelling. Little swelling was observed of the starch granules from the 16 oz chlorine per cwt treated flour. At 75°C this starch sample began to fade and disappear leaving only a small circular fragment. The control starch at this temperature was very light in color but was observed to be folding and overlapping one another with well defined edges visible for each granule. The control starch faded at 96°C.

#### Differential Scanning Calorimetry

The gelatinization transitions of starch isolated from chlorinated flours were studied with a Differential Scanning Calorimeter (DSC). The calorimeter was also used to determine the melting temperature

Table 4. Gelatinization Temperatures  
of Chlorinated Starches

Chlorine, oz/cwt Flour	Gelatinization, °C		
	Initiation	Mid point	Final
0	58	62	65
2	59	63	65
4	57	63	65
8	59	68	70
16	63	66	68



( $T_m$ ) range at which gelatinization occurred and the enthalpy involved in the transition.

Wheat starch isolated from chlorinated flour was heated in excess water and the thermograms shown in Fig. 6 were obtained. These thermograms are plots of heat flow as a function of temperature. Approximately equal weights of starch previously isolated from chlorine-treated flour (0 to 16 oz chlorine per cwt of flour) were measured in preweighed DSC pans. The weight ratio of water to starch was 3:1.

To distinguish the various transitions that will be described Donovan (1980) used the following rather arbitrary convention. The lowest temperature transition observed for all starches in excess water is the well known gelatinization transition, called here the (G) transition. For most starches, the G transition occurs in the temperature range of 65-75<sup>0</sup> C. When water is limiting, the crystalline portions of the granule undergo melting at higher temperatures known as  $M_1$ . An endotherm with both transitions have been provided from Donovan's work (1980) Fig. 7.

The wheat starch samples from flour treated with 0, 2, 4, and 8 oz chlorine per cwt of flour maintained a similar endotherm for the G transition. The endotherms observed for these four samples of starch occurred over approximately a 20<sup>0</sup>C temperature range (Table 5). The half-width of the endotherms remained unchanged and the specific enthalpies of gelatinization (Table 6) were constant within experimental error. The effect of chlorine on starch at the highest treatment level of flour was more striking. The endotherm was significantly broadened, and the  $T_m$  range increased about 20<sup>0</sup>C as well as the specific enthalpy of the transition.

Figure 6. Effect of chlorination on starch gelatinization  
in a 1:3 ratio with water

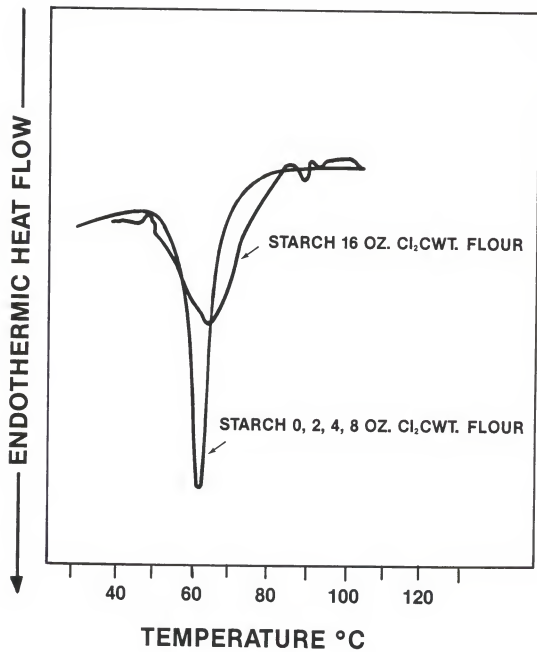


Figure 7. DSC thermograms of 3 day and 8 week prepared  
Nageli amyloextrins from Donovan's study (1980).

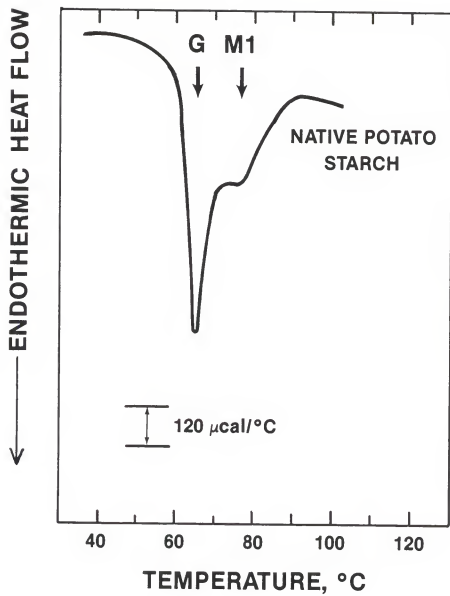


Table 5. Gelatinization Temperature Ranges from the DSC

oz Cl <sub>2</sub> /cwt	T <sub>o</sub> <sup>a</sup>	T <sub>p</sub> <sup>a</sup>	T <sub>c</sub> <sup>a</sup>	T <sub>m</sub> <sup>b</sup>
0	55	61	75	20
2	54	61	75	21
4	54	60	75	21
8	58	64	78	20
16	49	66	89	40

<sup>a</sup>Temperature gelatinization began (o), peaked (p), ceased (c).

<sup>b</sup>Melting temperature range.

Table 6. Heats of Gelatinization  
for Starches<sup>a</sup>

pH Flour	$\Delta H_G$ (Cal/g Starch) <sup>b</sup>
5.8	$2.5 \pm .08$
4.7	$2.5 \pm .04$
3.9	$2.5 \pm .10$
2.3	$2.5 \pm .08$
1.4	$3.3 \pm .02$

<sup>a</sup>Starches isolated from chlorinated flours.

<sup>b</sup>Mean  $\pm$  standard of error of the mean.  
n = 3.

Donovan (1980) explained that the transition depicted by the endotherm is due to melting of crystallites in the amorphous regions of the granule, which are destabilized when a solvent swells the granule. The sharpness of the transition, and the temperature at which it occurs, depend on the force exerted on the crystallites by the swelling and the coupling between the crystallites and the amorphous regions. When the crystallites are extensively "decoupled" from the amorphous network by acid treatment, the marked broadening of the melting transition, and its shift to higher temperatures gives a more accurate picture of their inherent stability, heterogeneity in size, and crystalline perfection. The constancy of the melting enthalpy of the starch samples from the 0, 2, 4, and 8 oz chlorine per cwt of flour indicate that the crystalline regions were affected little by the chlorine treatment, except in the highly treated starch where it is evident by the increased enthalpy that a change in crystalline structure occurred.

Similar observations to ours were made by Donovan (1980) when he prepared Nageli amyloextrins from potato starch treated with 15% sulfuric acid. The DSC was used to determine phase transitions characteristic of acid treated potato starch. The shorter acid treatment (3 days exposure to acid) merely shifted the endotherm for the G transition to higher temperature; the half-width of the endotherm was unchanged and the enthalpy of G was constant. The longer acid treated potato starch sample (8 weeks exposure to acid) had a more striking effect; the endotherm was significantly broadened and the endotherm peak temperature was  $9^{\circ}\text{C}$  higher than that for native starch but, the enthalpy of the transition remained unchanged. Donovan reasoned that when a significant fraction of the amorphous chains of the granule is



hydrolyzed, as in the 8 week sample, the heterogeneity of the crystalline region becomes evident in the broadening of the endotherm; with little to no loss of crystalline structure since the enthalpy is unchanged. The Nageli amylopectin from 3 days exposure to acid left a large degree of structure intact or a large degree of homogeneity as shown by the unchanged half width of the endotherm.

The difference between Donovan's (1980) and our present study is the difference in the enthalpy of his 8 week acid treated (15% sulfuric acid) starch sample and our highly chlorine-treated starch sample. Chlorine through its reaction with water forms hydrochloric acid and hypochlorite and thus has both hydrolyzing and oxidizing effects (respectively). In contrast, the sulfuric acid used by Donovan (1980) in preparation of Nageli amylopectins produces only hydrolytic reactions. The hydrolysis and oxidation may form dissimilar crystallites, thus giving higher enthalpies than those seen in Donovan's (1980) work. Since lipids are present in wheat starch but, not in potato starch, the starch lipids may also be involved in formation of dissimilar crystallites.

#### Viscograms of Cookie Crumbs

The viscograms of the cookie crumbs made from chlorinated flour of 0, 2, 4, 8, and 16 oz chlorine per cwt of flour are shown in Fig. 8. Little change was seen in the pasting characteristics of cookies made with flour pH 5.9 to 3.9 (0 to 4 oz chlorine per cwt of flour) as seen by the change in BU in Table 7. The cookies made with flour pH 2.3 and 1.4 (8 and 16 oz chlorine per cwt of flour) showed a loss of pasting ability.

Here again, the formation of Nageli-type amylopectins may be

Figure 8. Effect of chlorination on viscograms made with untreated and chlorine-treated cookie crumbs.

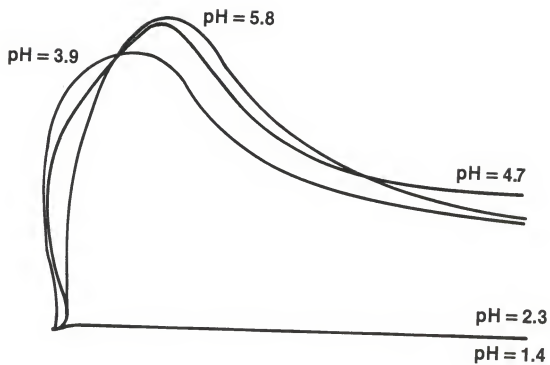


Table 7. Amylograph Indices

pH Flour	pH Cookie	BU <sup>a</sup>
5.8	8.3	630
4.7	8.1	610
3.9	8.0	560
2.3	7.7	-
1.4	5.4	-

<sup>a</sup>Brabender Units

apparent. Kainuma and French (1971) cited several properties of amyloextrins. One of these properties is the ability of the amyloextrins to dissolve readily in hot water to form a true solution rather than a paste. The amylograph data confirmed this conclusion and further supported the presence of Nageli-type amyloextrins.

To control the effect of low pH, the cookie crumb from the 8 oz treated flour was neutralized prior to heating in the amylograph. A loss of pasting ability did not change upon neutralization with 0.1 N NaOH, showing that the starch was altered by the chlorination process at that high level of treatment.

It is evident that the starch treated with 8 and 16 oz chlorine per cwt of flour had extensively modified properties to produce viscosities with essentially no pasting characteristics. The inability of the cookie crumb slurry to paste from the 8 and 16 oz chlorine per cwt of flour was attributable to the depolymerization of the starch by chlorine.

The depolymerization is not surprising. However, it is remarkable that the starch granule in flours treated with high levels of chlorine retained their integrity and birefringence as evident from microscopic observation in polarized light and their high order as indicated by the DSC results. All these characteristics support our conclusion that Nageli-type amyloextrins were formed.

#### Falling Number

The falling number was another method used to test the gel consistency from untreated and chlorine-treated flours by the time (sec) required for the plunger to fall through the gel. The thicker the gel, the more time the plunger takes to fall its distance through the gel.

The falling numbers (Table 8) for each level of chlorine-treated flour demonstrate an initial increase in gel consistency to 2 oz chlorine per cwt of flour, followed by a rapid weakening of gels at higher chlorine levels. Even though a small degree of pasting is evident from the flours in the falling number, the amylograph was not sensitive enough to record this phenomenon on the cookie crumb slurry. The loss in gel consistency was; however, in good agreement with the amylograph data.

#### Scanning Electron Micrographs

The Scanning Electron Microscope (SEM) scans the surface of the sample with an electron beam creating an image observed by the secondary electrons being emitted from the surface. Photomicrographs of the images observed can be made fairly quickly with a Polaroid camera.

The surface of starch granules isolated from defatted cookie dough and crumbs made with untreated (0 oz chlorine per cwt of flour) and treated (2-16 oz chlorine per cwt of flour) were viewed at 500 and 1000 times magnifications with the SEM. Figure 9 shows scanning electron micrographs of defatted starch from cookie doughs and Fig. 10 from defatted cookie crumbs made with flours treated with increments of chlorine. Occasional fractures (arrow) were observed in the starch from the highly treated flour which may be due to chlorine treatment.

#### Cookie Baking

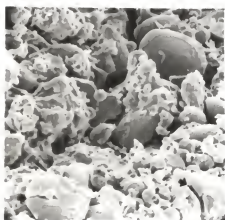
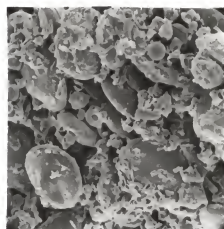
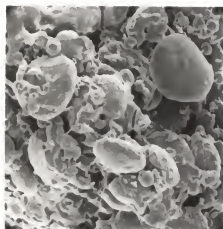
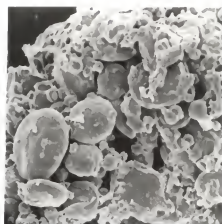
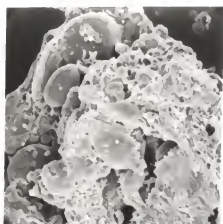
The spread, color, and surface cracking characteristics of the cookies baked with increasing increments of chlorinated flour are shown in Fig. 11. The pH of the flours, doughs, and cookies as well as the cookie diameter and thickness of the cookies are shown in Table 9. Slight and decreasing differences were detected in the pH levels of the dough and cookie as the level of chlorine increased. These small

Table 8. Effect of Chlorination on Pasting  
as Measured by Falling Number

Chlorination Level (oz/cwt)	Falling Number (sec)
0	429
2	453
4	289
8	111
16	62

- Figure 9A. Scanning electron micrograph of starch from defatted cookie structure made with untreated flour, top left.
- Figure 9B. Scanning electron micrograph of starch from defatted cookie structure made with 2 oz chlorine per cwt of flour, top right.
- Figure 9C. Scanning electron micrograph of starch from defatted cookie structure made with 4 oz chlorine per cwt of flour, middle left.
- Figure 9D. Scanning electron micrograph of starch from defatted cookie structure made with 8 oz chlorine per cwt of flour, middle right.
- Figure 9E. Scanning electron micrograph of starch from defatted cookie structure made with 16 oz chlorine per cwt of flour, bottom left.





- Figure 10A. Scanning electron micrograph of starch from defatted cookie dough made with untreated flour, top left.
- Figure 10B. Scanning electron micrograph of starch from defatted cookie dough made with 2 oz chlorine per cwt of flour, top right.
- Figure 10C. Scanning electron micrograph of starch from defatted cookie dough made with 4 oz chlorine per cwt of flour, middle left.
- Figure 10D. Scanning electron micrograph of starch from defatted cookie dough made with 8 oz chlorine per cwt of flour, middle right.
- Figure 10E. Scanning electron micrograph of starch from defatted cookie dough made with 16 oz chlorine per cwt of flour, bottom left.

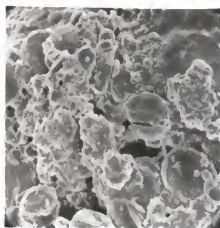
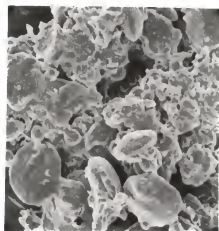
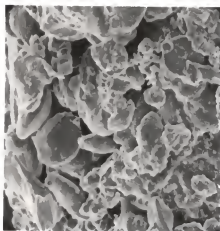
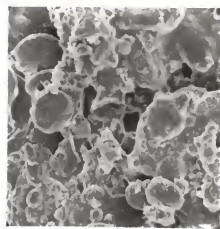
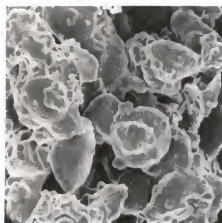


Figure 11. Cookies baked with varying levels of chlorinated flour.

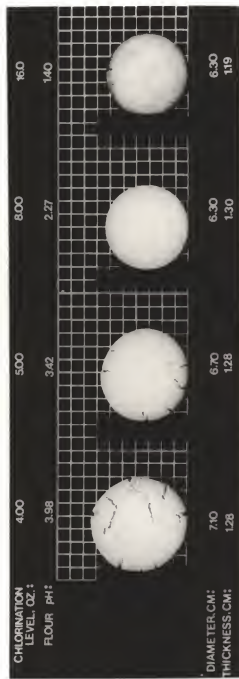
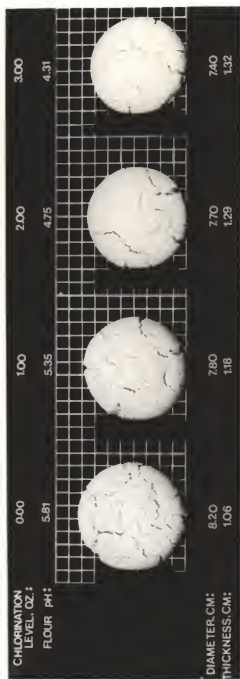


Table 9. Effect of Chlorination on pH, Spread, and Thickness of Cookies

Cl <sub>2</sub> Level oz/cwt	Flour	pH Dough	Cookie	Cookie Spread (cm)	Thickness (cm)
0	5.8	8.1	8.3	8.2 $\pm$ .01	1.1
2	4.7	7.8	8.3	7.7 $\pm$ .01	1.2
4	3.9	7.8	8.1	7.1 $\pm$ .03	1.3
8	2.3	7.6	7.7	6.3 $\pm$ .02	1.3
16	1.4	6.5	5.4	6.3 $\pm$ .02	1.3

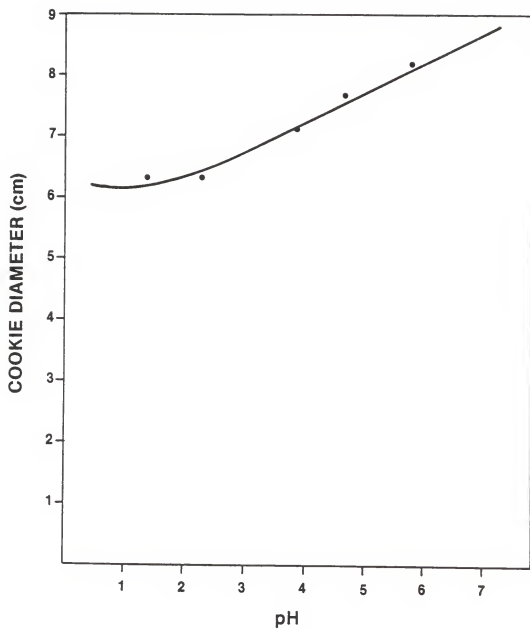
differences are attributable to the buffering action from the NFDM solids,  $\text{NaHCO}_3$ , and the flour. Cookie thickness showed no significant differences. A gradual increase in cookie diameter occurred as the level of chlorination decreased as indicated by pH values. This can also be seen as an indirect relationship between the increased acidity of flour to cookie diameter in Fig. 12.

In conclusion, the results of this study indicate to the cookie manufacturer that:

1. Chlorinated flour reduces cookie spread and diminishes normal cookie surface cracking.
2. The change of dough rheology affected by increasing levels of chlorination are: increased dough stickiness and a weakening of dough consistency.
3. Heterogenous hydrolysis effected by chlorine in the amorphous starch regions formed Nageli amyloextrins as indicated by retention of birefringence detected by polarized microscopy, high order as indicated by the DSC results, and the formation of a true solution rather than a paste as seen by the amylograph.

Figure 12. Relationship between the pH levels of chlorinated flour to cookie diameter.  $r = .99$  from second order regression.





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THE FUNCTIONALITY OF A CHLORINATED SOFT WHEAT  
FLOUR IN A COOKIE SYSTEM

by

CONSTANCE K. BACHOFER

B.S., Kansas State University, 1984

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AN ABSTRACT OF A MASTERS THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Grain Science

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1986

Soft wheat flour chlorinated to substantially lower pH values than cake flour, is becoming a common ingredient in cookie production for reduction of cookie spread. The objective of the investigation was to define the functionality of chlorinated flour in a cookie system. Flour treated with varied amounts of chlorine (0-16 oz chlorine per cwt of flour) was tested by physicochemical methods, SEM, and baking tests.

Farinograms and alveograms of flours showed initial strengthening of dough with treatment up to 4 oz chlorine per cwt of flour, followed by subsequent weakening of doughs. Viscograms of cookie crumb-water suspension showed similar pasting characteristics at low treatment levels; when treated below pH 4.0, the hot paste consistency was reduced, especially at the highest treatment level pH 1.4. This change in pasting characteristics was attributed to formation of Nageli-type amyloextrins by heterogenous hydrolysis effected by chlorine which attacks preferentially the amorphous starch regions. This conclusion was supported by other observations: the granules retained birefringence even when treated with 16 oz chlorine per cwt of flour. DSC showed an enthalpic peak, SEM showed little change in the granule. DSC studies indicated constant enthalpies up to pH 2.3; at highest treatment level pH 1.4, energy requirement increased and the peak broadened, indicating formation of heterogenous crystallites from the starch fragments produced by the action of chlorine. Baking tests demonstrated gradual reduction in cookie spread.

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